

Study of Degradation of Polystyrene, Using Infrared Spectrophotometry

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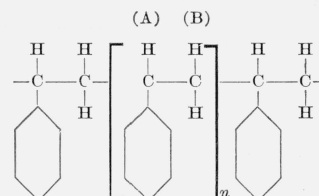
Since polystyrene is a widely used plastic and styrene is an integral part of the most widely used synthetic rubber (GR-S), it appears necessary to know something of the process of degradation of polystyrene to assist in interpreting the degradation of these materials in service. Polystyrene films were exposed to heat at 100° C in a forced-draft air oven and to ultraviolet radiant energy at 60° C in air. Chemical structural changes in the polymer as a result of these treatments were analyzed by study of the infrared spectra between 2 and 16 microns, obtained with a Baird recording infrared spectrophotometer. Ultraviolet exposure for 200 hours resulted in absorptions at 2.9 and 5.8 microns, which are attributed to hydroxyl and carbonyl groups, respectively. Heating of the film for 270 hours at 100° C produced no significant change in the infrared spectrum. Prolonged heating at 125° C resulted in the destruction of the films by flow. The literature and theory on the degradation of polystyrene are discussed. Several mechanisms are postulated to account for the production of hydroxyl and carbonyl products in the polymer.

1. Introduction

The hydroperoxide theory of the oxidation of olefinic systems, which resulted from studies by Farmer and his coworkers [1, 2, 3],¹ has led to various attempts to explain the oxidation and degradation of polymeric materials with related chemical structure [4 to 7]. According to this theory, hydroperoxidation occurs on the carbon atom alpha to the double bond. Although the complex decomposition of hydroperoxides with heat and light is not understood completely, it is thought that the hydroperoxide is converted to hydroxyl and there is some evidence that carbonyl may also be formed [5, 8]. Cole and Field [8] have applied these theories to the oxidation of butadiene-styrene copolymers and other elastomers and have suggested that the formation of carbonyl and hydroxyl absorptions in the infrared spectra, which they found, is a result of the breakdown of hydroperoxides. Work in this laboratory has verified that hydroxyl and carbonyl absorptions occur in the infrared spectra of butadiene-styrene copolymer (75:25) as a result of exposure at 100° C in an air oven and to ultraviolet radiant energy at 60° C in air.

Since polystyrene is a widely used plastic and styrene is also an integral part of butadiene-styrene elastomeric copolymers, it appears necessary to know something of the mechanism of the oxidation of polystyrene to assist in interpreting the degradation in service of this plastic and of the synthetic rubber-like materials containing styrene.

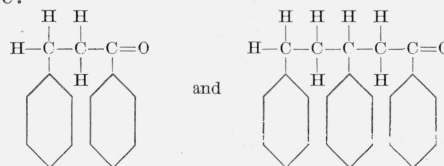
The following structure is generally accepted and thermodynamically likely as predominant in polystyrene:



where n determines the molecular weight of the particular polystyrene and is dependent on the conditions of polymerization. This gives polystyrene a relatively simple chemical structure to be considered in regard to degradation. The components of the chemical structure may be divided into three parts: (1) The benzene ring, (2) the tertiary carbon atom bearing a single hydrogen atom (A) and attached to the benzene ring, and (3) the methylene connecting bridges in which the secondary carbon atom holds two hydrogen atoms (B).

It is generally agreed that the C—H bond energy values are in the order primary greater than secondary greater than tertiary. The C—H bond energy is reduced when the hydrogen atom is attached to a carbon atom adjacent to a double bond [9]. From oxidation studies on simple hydrocarbons, it appears that a hydroperoxide group is likely to be formed at site (A).

Staudinger and Steinhöfer [10] showed that the unsaturated di- and tri- styrene fractions obtained on high vacuum distillation of polystyrene were oxidized by glacial acetic acid containing chromic trioxide with the formation of ketones of the following type:



¹ Figures in brackets indicate the literature references at the end of this paper.

Jellinek [11] suggested that the results of thermal degradation of polystyrene in the presence of oxygen indicate that a hydroperoxide mechanism may be responsible for the degradation. Although the infrared absorption spectrum of polystyrene is available in the literature [12, 13], infrared techniques have apparently not been used to follow the degradation of polystyrene.²

In the investigation described in this report polystyrene films were exposed in the presence of air to heat and to ultraviolet radiant energy and changes in the chemical structure of the polymer as a result of the treatments were detected by infrared spectrophotometry. Infrared analysis is suitable for this study since both the hydroxyl and carbonyl groups, which might be expected on oxidative degradation, have strong absorptions in the infrared region and are known to occur at approximately 3μ and 5.7 to 6.0μ , respectively, [14, 15]. The hydroxyl and carbonyl groups may be situated independently on the polymer molecule or be adjacent to each other as in carboxyl groups.

2. Materials

The samples of polystyrene studied are described in table 1. Samples A, B, C, D, E, E1, and G1 are commercial resins that do not contain any compounding ingredients. These samples were not subjected to any purification procedures but were used as received.

TABLE 1. Description of samples of polystyrene

Sample designation	Approximate molecular weight ^a	Average oxygen content ^b
		Percent
A	295,000	0.048
B	340,000	.066
C	290,000	.064
D	370,000	.033
E	360,000	.26
E1	290,000	.27
G1	230,000	.12
^c X	^d 230,000	.11

^a Weight average molecular weight as determined by light scattering (unpublished work of William A. Crouse).

^b The oxygen content was determined by the direct method of Walton, McCulloch, and Smith (W. W. Walton, F. W. McCulloch, and W. H. Smith, Determination of small amounts of oxygen in organic compounds, J. Research NBS **40**, 443 (1948) RP1889). The samples were dried in a stream of purified helium at 100° C for 16 hr before being analyzed.

^c The molecular weight and oxygen content were determined after purification. The oxygen content before purification was 0.13%.

^d Number average molecular weight as determined by osmotic pressure (unpublished work of Guy A. Hanks).

The sample designated X was prepared by polymerizing purified monomer without catalyst or solvents in a nitrogen atmosphere at 120° C for 48 hr. It was subjected to the following purification prior to use: The sample was dissolved in benzene and precipitated with methanol, and the liquid was decanted. This treatment was repeated. The twice-

precipitated material was dissolved in benzene and the solution frozen. The benzene was removed with a vacuum pump while the frozen mixture was slowly brought to 24° C. The light fluffy sample was kept under vacuum while being raised to 60° C and finally held there for 24 hr to remove essentially all the volatile materials. The sample was then stored in a dark glass bottle until used. This procedure was designed to remove impurities, low molecular weight polymer, and monomer. Other studies showed that the dried product contained less than 1 percent of benzene. Although the purified sample X was considered to be polystyrene hydrocarbon, it is evident from the data shown in table 1 that some oxygen is incorporated in the polymer molecules in spite of the precautions taken to exclude it.

Samples C, E1, and X were studied more extensively than the others. Samples C and E1 are representative of the two types into which the commercial samples can be classed according to their infrared absorption spectra. Sample C is representative of samples A, B, C, D, and G1. Samples E and E1 are similar.

3. Film Preparation

Films of various thicknesses ranging from 0.0009 to 0.010 in. were made for the tests. The thinner films were made from 5- and 10-percent solutions of the sample in distilled toluene or benzene. The solution was poured on a clean, level piece of plate glass and spread to an even thickness with a doctor blade. A dust shield was placed above the solution, and the film was allowed to form in air. When the film was dry, the plate was immersed in water and the film floated from it. In most cases the film was then dried in a vacuum chamber for about 8 hr followed by exposure to the room atmosphere until used.

The thicker films were made from 15-percent or more concentrated solutions of the samples in distilled solvent. The amount of solution necessary to form a film of the desired thickness was poured into a brass ring which was laid on a clean, level piece of plate glass. A dust shield was placed above the solution in the ring and the film allowed to form in air. Slower drying was necessary for uniform film formation when highly volatile methyl ethyl ketone was used and, therefore, the whole assembly was placed in a desiccator with two outlets open to the air. When the film was dry, the plate was immersed in water, the ring jarred loose from the plate, and the film floated from the plate. The film was then dried in a vacuum chamber for about 8 hr and stored in air until used. Nevertheless, some solvent remained in the film resulting in carbonyl absorption in the infrared spectrum, and the use of methyl ethyl ketone as a solvent was abandoned. Some toluene and benzene were retained by the films, but their presence did not interfere with the observation of infrared absorptions caused by carbonyl or hydroxyl resulting from degradative treatment.

Thickness measurements of the films were made in some cases with a Mikrokator gage that has a scale

² Since this paper was written, Matheson and Boyer reported at the Chicago meeting of the American Chemical Society in September 1950, concerning work using infrared absorption to follow carbonyl formation in polystyrene.

range of 0.0014 in. with graduations of 0.00002 in. In other cases the films were measured with a Carson electronic micrometer or with an ordinary micrometer.

4. Experimental Methods

4.1. Measurement of Absorption in the Infrared Region

The infrared absorption spectra of the films were measured between 2.0 and 16.0 μ with a Baird recording infrared spectrophotometer with a sodium chloride prism [16]. This instrument is a double-beam type operating on the optical null principle. Using the atmosphere as a reference, the infrared absorption at each wavelength was recorded through a bolometer, amplifier, and mechanical drive system. A graph of percentage transmission of the film versus wavelength is obtained by this method. Changes in chemical structure of the polystyrene film on exposure to degradative treatment were observed by comparing the infrared absorption spectrum before treatment with the spectrum of the same film after treatment.

The use of the Baird spectrophotometer on this project was necessarily intermittent. Because of changes in the sensitivity of the instrument introduced between periods of use on this project, some of the spectra show differences in resolution and intensity of the bands. These spectra have not been superimposed for comparison, as have the others. No attempt is made in this report to compare or observe minor changes in the infrared absorption spectra, and changes in the absorption bands resulting from the various treatments are considered qualitative rather than quantitative.

4.2. Heat and Ultraviolet Exposure of Films

The film holders, in which the films were exposed to the various treatments, were designed to fit the aperture of the Baird recording spectrophotometer. These holders were made of chromium-plated brass and had a 2 $\frac{1}{8}$ -in.-diameter aperture for the film.

Polystyrene films inserted in these holders were exposed at 100° C in a laboratory forced-draft oven. Ultraviolet exposure in air was made by placing the films on a revolving table 6 in. from an S-1 sunlamp.³ The temperature of the air at the revolving table was about 60° C. This sunlamp equipment is described in Method No. 6021 of Federal Specification L-P-406a [17].

4.3. Outdoor Exposure of the Films

Several films inserted in metal holders were exposed outdoors in Washington, D. C., on racks at an angle of 45°, facing south. This exposure was started in early December 1949, and was continued 5 months, through April 1950.

³ It is recognized that the radiant energy from the S-1 sunlamp includes infrared and visible wavelengths as well as those of the ultraviolet. However, it is assumed that in the short periods of exposure used in these experiments the ultra-violet radiant energy is chiefly responsible for the observed effects.

5. Results

The infrared absorption spectra of polystyrene films, both untreated and after exposure to heat and to ultraviolet radiant energy in the presence of air, are shown in figures 1 to 8, inclusive. The many individual absorption bands of polystyrene, as shown in the untreated films (figs. 1 to 4, inclusive), are not discussed in this report. Interpretation is attempted only in the case of bands in which changes are observed as a result of degradative treatment.

5.1. Untreated Films

A comparison of the infrared absorption spectra of untreated films of samples A, B, C, D, E, E1, and G1 was made as the initial phase of this work. The absorption spectra showed that samples E and E1 could be differentiated from samples A, B, C, D, and G1 by a comparison of absorption at 5.75 μ for films at least 0.0009 in. thick. Infrared absorption spectra of untreated films of samples C and E1 are shown in figures 1 and 2, respectively, as representative of the two classes. Comparison of these spectra shows that sample E1 has greater absorption at 5.75 μ , indicated by an arrow on the graph. Absorption in this region generally results from the type of structures represented by

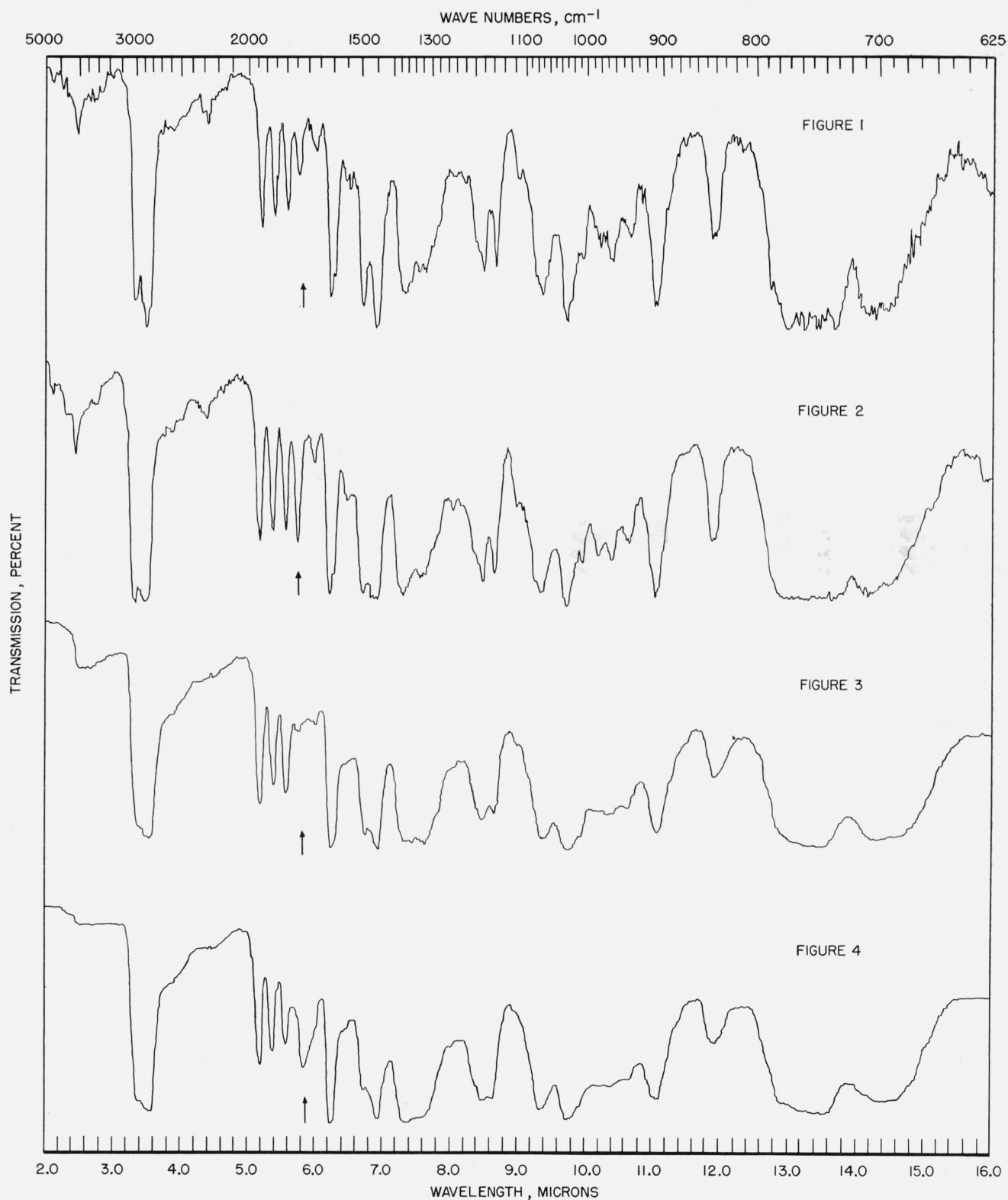


where Y is R, H, OR, or OH.

The infrared absorption spectra of untreated films of sample X are shown in figures 3 and 4, the Baird spectrophotometer having been set at a low sensitivity. Figure 3 shows the spectrum of a film of sample X cast from a benzene solution. The absorption at 5.75 μ is very slight. Figure 4 shows the spectrum of a sample X film cast from methyl ethyl ketone solution. The stronger absorption at 5.85 μ is attributed to the presence of some residual methyl ethyl ketone in the film.

5.2. Films Exposed to 100° C in an Air Oven

Films of polystyrene samples C, E1, and X were exposed for various periods in a laboratory forced-draft air oven at 100° C. No extensive changes in the infrared absorption spectra of the films were observed as a result of this treatment, that is, no new bands were created or old bands removed. Figure 5 shows the infrared absorption spectra of a film of sample X after 200 hr at 100° C in air superimposed on the absorption spectra of the same film after 50 hr at 100° C in air. Only insignificant changes in the absorption spectra are shown as a result of this exposure. No chemical changes have occurred that are detectable by infrared spectrophotometry. This is also representative of the results obtained with films of samples C and E1 exposed for 270 hr. These results differ from those suggested by Jellinek [11] for pyrolytic conditions.



Infrared absorption spectra of untreated polystyrene films

Figure	Sample	Thickness	Solvent	Figure	Sample	Thickness	Solvent
1-----	C	<i>in.</i> 0.007	Toluene	3-----	X	<i>in.</i> 0.007	Benzene
2-----	E1	.007	Toluene	4-----	X	.007	Methyl ethyl ketone

5.3 Films Exposed to Ultraviolet Radiant Energy at 60° C in Air

A comparison of the absorption spectrum of sample X after 50 hr of exposure to ultraviolet radiant energy at 60° C in air with the absorption spectrum after 200 hr at these conditions is shown in figure 6. Definite increases in absorption at approximately 2.9 and 5.8 μ after 200 hr of treatment indicate the formation of hydroxyl and carbonyl groups, respectively.

The absorption spectrum of an untreated film of sample C is compared in figure 7 with the absorption spectrum of the same film after 200 hr of exposure to ultraviolet radiant energy at 60° C in air. The formation of hydroxyl and carbonyl groups is indicated by the definite increases in absorption at 2.9 and 5.8 μ , respectively. The elimination of the absorption at 13.7 μ is attributed to loss of residual toluene solvent. A rather general increase in the background absorption results from the treatment.

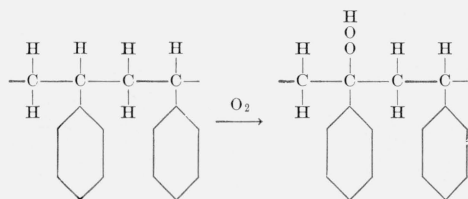
Comparison of figures 7 and 8 shows that polystyrene sample E1 exhibits similar changes in infrared absorption when exposed to ultraviolet radiant energy in air.

5.4. Films Exposed to Outdoor Weathering

In order to determine whether outdoor weathering would produce hydroxyl and carbonyl groups in polystyrene, films of samples A, E1, and X were exposed outdoors for 5 months in Washington, D. C. Measurements made every month show that oxidation occurs progressively in all three samples and produces hydroxyl and carbonyl groups. The change in absorption attributed to the formation of hydroxyl groups is relatively weak. The superimposed initial and 4-month transmission curves for samples X and E1 are presented in figures 9 and 10, respectively.

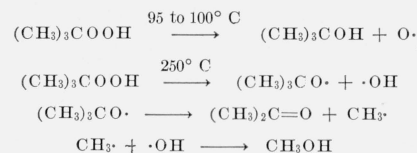
6. Discussion of Results

The infrared absorption spectra show that hydroxyl and carbonyl groups are formed in the polystyrene polymer on exposure to ultraviolet radiant energy from both natural and experimental sources. The oxidation resulting in these products probably occurred through the formation of a hydroperoxide on the tertiary carbon in the polystyrene chain. This mechanism can be postulated as follows:

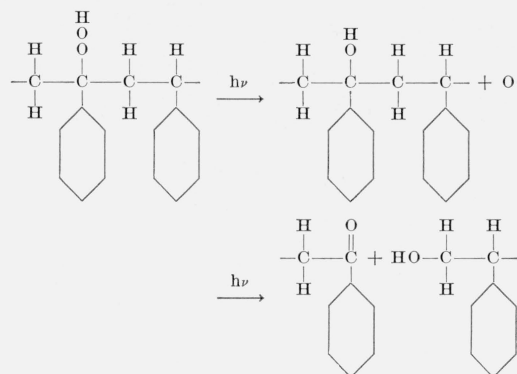


The hydroxyl and carbonyl groups could result from subsequent breakdown of this hydroperoxide under ultraviolet radiant energy.

George and Walsh [18] have studied the decomposition of tertiary alkyl peroxides. Milas and Surgenor [19] have shown that the following scheme can be applied to the thermal decomposition of tertiary butyl hydroperoxide:



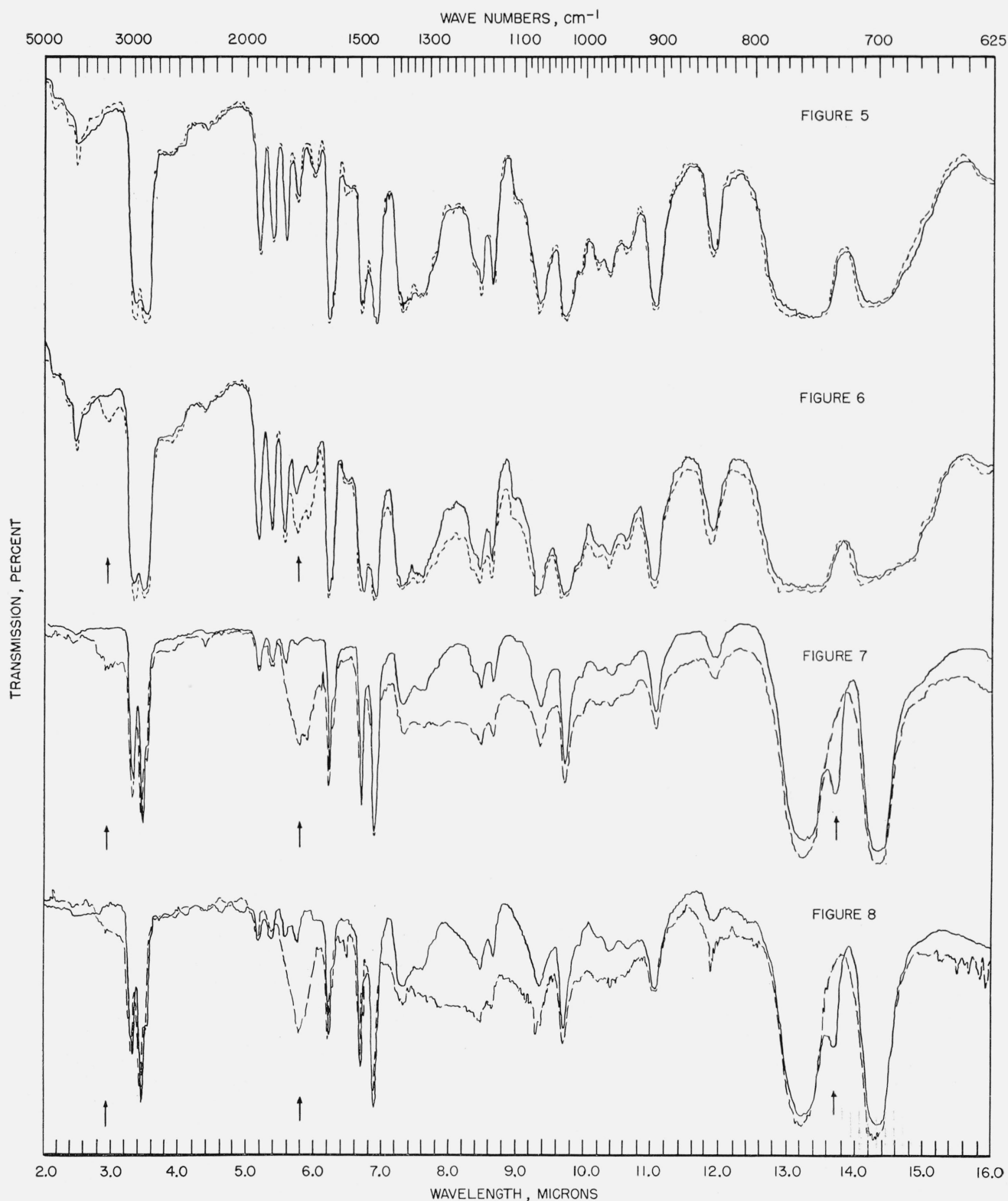
The decomposition of the tertiary hydroperoxides in polystyrene may lead to carbonyl and hydroxyl groups by a similar mechanism:



This mechanism would also presumably be of a free radical nature.

Although no evidence of oxidation was observed in the infrared spectra after heating the polystyrene films for 270 hr at 100° C in air, this does not necessarily infer that longer exposure or higher temperature would not produce oxidation resulting in hydroxyl and carbonyl groups. The infrared pattern after 100 hr at 125° C in an air oven showed no extensive changes from the initial pattern, although the films were starting to sag and flow. Continued exposure resulted in destruction of the films due to flow and development of holes. Films exposed to 150° C in an air oven (after previous exposure to 100° C for 270 hr) developed holes and flowed after 1 hour's treatment. The necessary energy to cause oxidation is supplied, however, on exposure to ultraviolet radiant energy at a temperature as low as 60° C. The carbonyl group absorption is definitely present after 70 hr of exposure and the hydroxyl absorption after 100 hr. This is compatible with the hypotheses of Jellinek and others [10 and 11] that hydroperoxide formation may be responsible for the degradation of polystyrene.

Assuming random scission, the formation of carbonyl groups would decrease the molecular weight of the polymer since the formation of each carbonyl would cause a break in the chain molecule. An increase in solubility would be expected as a result. Ultraviolet-treated samples of C and E1 in table 2 show that oxidation resulting in the formation of hydroxyl and carbonyl groups is accompanied by an



Infrared absorption spectra of treated polystyrene films

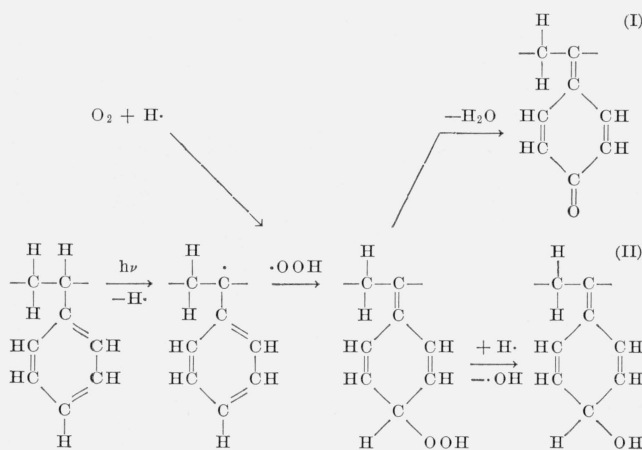
Figure	Sample	Thickness	Solvent	Treatment	Figure	Sample	Thickness	Solvent	Treatment
5-----	X	0.007 in.	benzene	—, 50 hr at 100° C in air; ---, 200 hr at 100° C in air.	7-----	C	0.001 in.	toluene	—, Untreated; ---, 200 hr S-1 sunlamp at 60° C.
6-----	X	.007	benzene	—, 50 hr S-1 sunlamp at 60° C; ---, 200 hr S-1 sunlamp at 60° C.	8-----	E1	.001	toluene	—, Untreated; ---, 200 hr S-1 sunlamp at 60° C.

TABLE 2. Solubility of polystyrene samples

Sample designation	Treatment	Solvent used	Thickness of film	Apparent solubility ^a	Condition of film	Color of film
			<i>in.</i>			
X	Untreated	a. Methyl ethyl ketone	0.0009	Soluble immediately	Not brittle	Colorless.
		b. do	.007	Soluble	Brittle	Do.
C	do	c. Benzene	.007	do	do	Do.
El	do	Toluene	.001	Soluble immediately	Not brittle	Do.
		do	.001	do	do	Do.
X	200 hours at 100° C in air	a. Methyl ethyl ketone	.008	do	Slight flow; brittle	Do.
		b. Benzene	.007	do	do	Do.
C	238 hours at 125° C in air	Toluene	.010	Soluble	Film not intact; evidence of flow; brittle.	Slightly yellow.
El	216 hours at 125° C in air	do	.007	do	do	Do.
X	200 hours S-1 sunlamp at 60° C in air	a. Methyl ethyl ketone	.007	Soluble immediately	Very brittle	Yellow.
		b. Benzene	.008	do	do	Do.
C	do	Toluene	.001	Insoluble (yellow particles remain).	Splitting; very brittle	Do.
El	do	do	.001	Some insolubility (yellow particles remain).	do	Do.

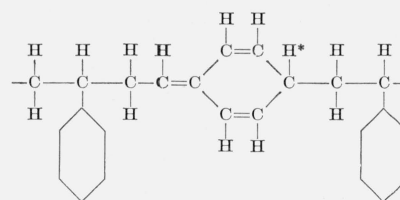
^a Soluble immediately=soluble within 5 min with shaking; soluble=soluble within approximately 1 hr with occasional shaking.

apparent decrease in solubility. The formation of carbonyl groups may, therefore, not be concomitant with chain scission; or a competitive cross-linking may be overshadowing chain scission. It is also possible that the groups in question are formed by reaction at chain ends or by oxidation of the benzene ring. The latter type of oxidation can be postulated as follows:



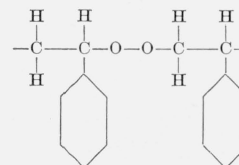
The (I) structure, which is basically a quinone, contains the requirements such as conjugated double bonds and carbonyl conjugate with a double bond to explain the discoloration of the polymer observed on exposure to ultraviolet radiant energy. On the other hand, a sufficient number of quinoid carbonyl groups to account for the absorption at 5.8μ in figures 6, 7, and 8 after treatment should also be accompanied by noticeable absorptions characteristic of the quinoid structure. The absence of noticeable differences at 6.2μ is not very good negative evidence, since the absorption may be obscured by that of the unchanged benzene structure.

If it is assumed that some benzene rings may exist as part of the linear polymer chain, the following structure is suggested for the polymer:

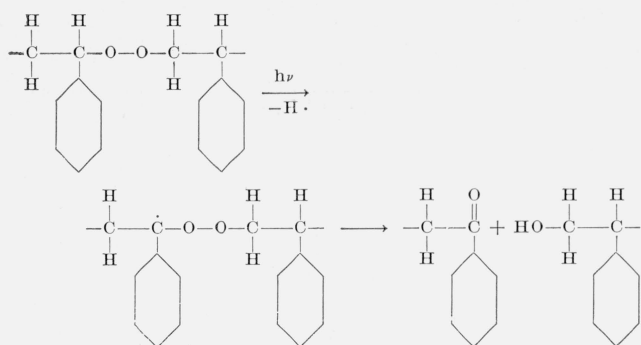


The hydrogen of a tertiary carbon atom (*) is available for the hydroperoxidation as are double bonds in a ring that may be oxidized singularly without subsequent scission of the linear chain. However, the likelihood of such a structure forming in the polymer is very slight, and consequently the amount would be too small to account for the results obtained in this study; but it might be considered as a contributing influence. Oxidation at the double bond also seems probable in the structures (I) and (II).

Table 1 shows that the polystyrenes used in this study contain oxygen. This oxygen was probably introduced in the polymerization stage. One possible structure likely to be formed when the double bond of the monomer is opened in the presence of oxygen is as follows:

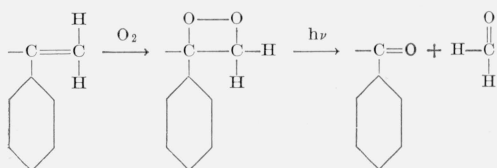


With oxygen in this form in the polymer, the production of carbonyl and hydroxyl groups on exposure to ultraviolet radiant energy can be postulated as follows:

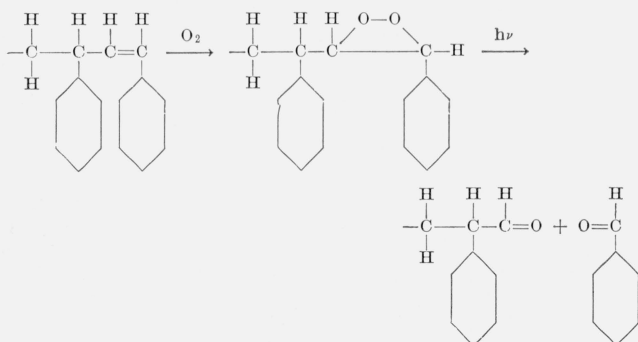


This process also causes a decrease in molecular weight and may result in products similar to those postulated for the breakdown of hydroperoxide on the tertiary carbon atom.

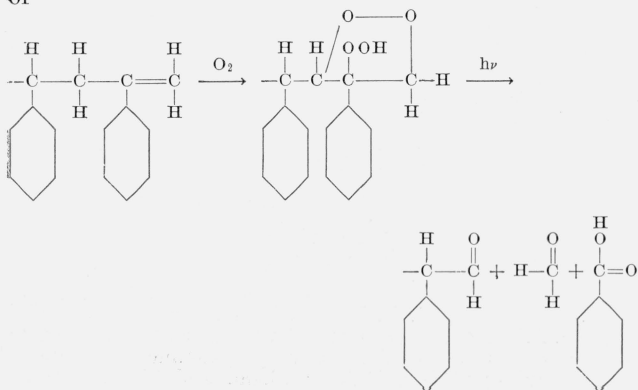
Since sample X was polymerized from purified styrene in a nitrogen atmosphere, the oxygen may have been taken on after the polymerization stage. In this case, as well as for all the other samples, it may be that the oxygen will react with an unsaturated group at the end of a molecule to give the following structures, which may react on exposure to ultraviolet radiant energy as indicated:



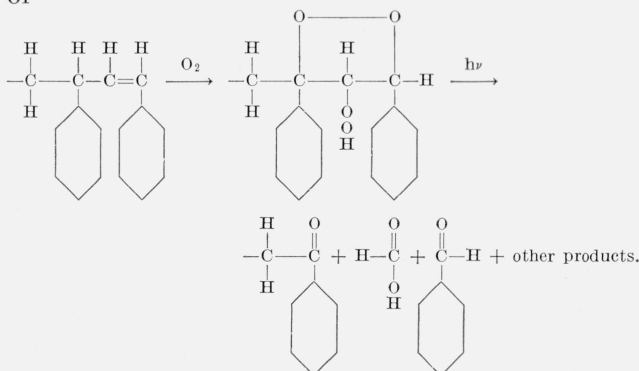
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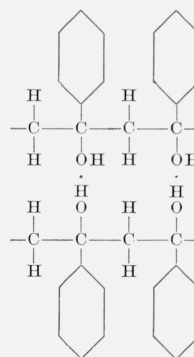


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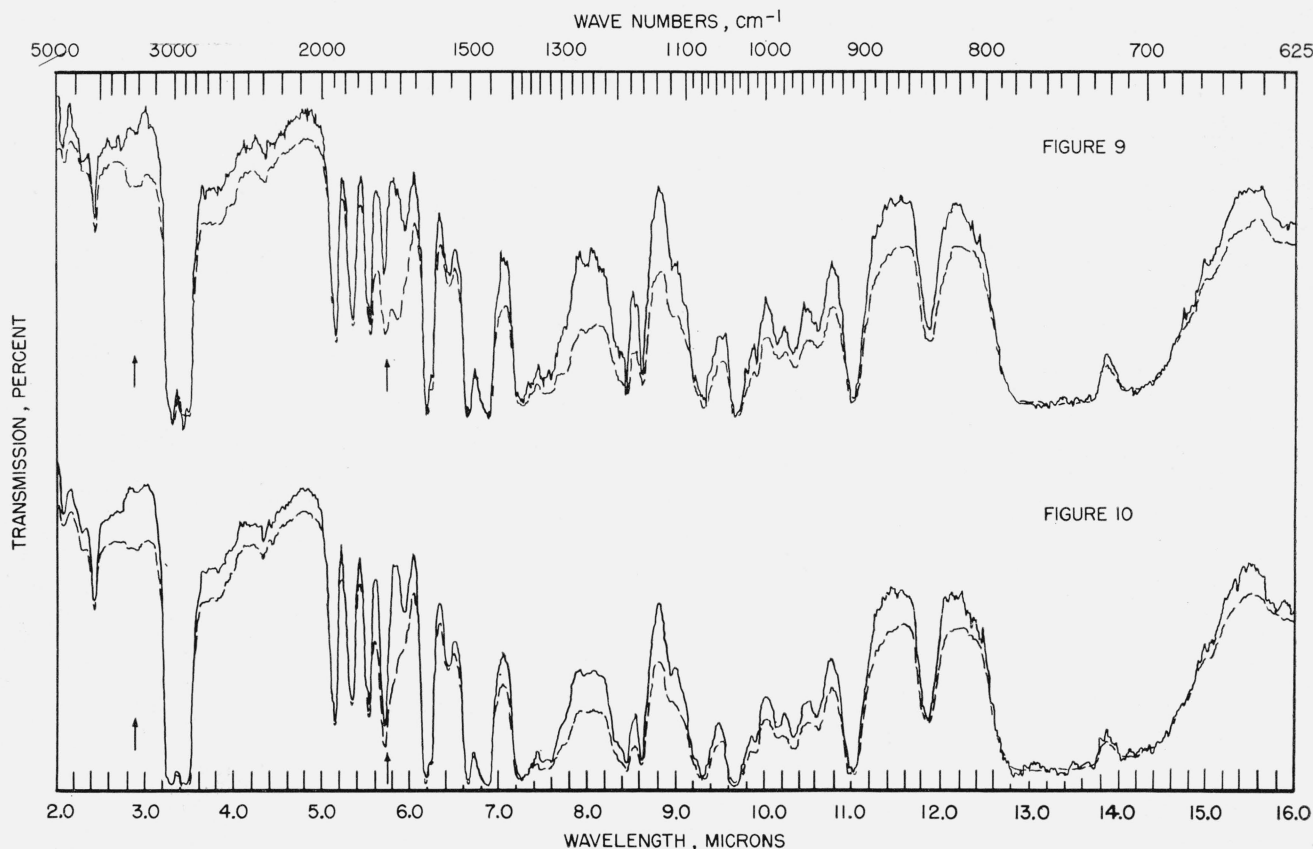


All these mechanisms show that the oxidation of a double bond chain end is likely to produce a carbonyl group on the end of the polymer molecule. The diperoxide structure given above has been suggested by Bolland and Hughes for squalene [20]. Chain end oxidation could be expected to produce a relatively smaller number of carbonyl groups than hydroperoxide chain scission, and the latter would appear to conform better to the solubility effects for sample X in table 2.

In regard to the hydroxyl absorption in the infrared spectra, the absorption band is found in the region of hydrogen-bonded hydroxyl rather than at the somewhat shorter wavelength attributed to free hydroxyl [14, 15]. Intermolecular bridging between hydroxyls in adjacent chains seems probable as shown below:



This suggests the possibility of crosslinking of chains by loss of water forming the ether linkage between chains. Also it is possible to postulate both peroxide and carbon to carbon crosslinking at the carbon bearing the tertiary hydrogen. Such crosslinking and intermolecular bridging would help to explain the increased brittleness and decreased solubility of the polystyrene on exposure to ultraviolet radiant energy. With sufficient fundamental background data it might be possible to identify some of the existing absorption bands in the spectrum of ultraviolet-treated films as due to ether or peroxide linkages.



Infrared absorption spectra of treated polystyrene films

Figure	Sample	Thickness	Solvent	Treatment
9-----	X	<i>in.</i> 0.007	toluene	—, Untreated; -----, 4 months' outdoor exposure.
10-----	E1	.008	toluene	—, Untreated; -----, 4 months' outdoor exposure.

7. Summary and Conclusions

Polystyrene films oxidize when exposed to ultraviolet radiant energy in air. Absorptions characteristic of hydroxyl and carbonyl groups are found in the infrared spectra of the exposed films.

Exposure of polystyrene films in an air oven at 100° C for 270 hr does not result in hydroxyl or carbonyl absorption in the infrared spectra. Oxidation resulting in the formation of these groups might occur on longer exposure or exposure at higher temperature; however, the films were destroyed by flow at prolonged exposure at 125° C.

The degradation of polystyrene film by ultraviolet radiant energy in the presence of air probably occurs through the formation of a hydroperoxide and subsequent breakdown and rearrangement to give hydroxyl and carbonyl products in the polymer. These carbonyl groups are most likely in the form

of ketones; however, by means of the infrared spectra it is not possible to differentiate between the carbonyls of the ketone, aldehyde, and acid, all of which might be present to some degree.

This investigation was sponsored by and conducted with financial assistance from the Office of the Quartermaster General, Department of the Army.

The courtesy of C. J. Humphreys, Chief of the Radiometry Section, in making the Baird Recording Spectrophotometer available for this work is appreciated.

The work of E. K. Plyler of the Radiometry Section on another project, in which he found that the commercial grades of polystyrene are of two types as shown by differences in absorption at 5.75 μ , was used as a basis for selecting samples C and E1 for this work; his help and encouragement are appreciated.

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